

# REVIEW OF CO<sub>2</sub> CAPTURE TECHNOLOGIES AND SOME IMPROVEMENT OPPORTUNITIES

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## ABSTRACT

Reducing CO<sub>2</sub> emissions for addressing climate change concerns is becoming increasingly important as the CO<sub>2</sub> concentration in the atmosphere has increased rapidly since the industrial revolution. Many mitigation methods, including CO<sub>2</sub> sequestration and novel CO<sub>2</sub> utilization, are currently under investigation. Most of these processes require CO<sub>2</sub> in a concentrated form. However the CO<sub>2</sub> from large sources such as fossil fueled power plants is mixed with nitrogen, water vapor, oxygen, and other impurities. A typical CO<sub>2</sub> concentration from coal fired power plants is around 15 %, while CO<sub>2</sub> concentrations for natural gas fired plants are less than 10 %. Therefore, capturing CO<sub>2</sub> from flue gas is an important common link for many mitigation methods.

The current commercial operations for capturing CO<sub>2</sub> from flue gas use a chemical absorption method with Monoethanol Amine (MEA) as the sorbent. The method is expensive and energy intensive. The cost of capturing a ton of CO<sub>2</sub> including removing impurities and compressing CO<sub>2</sub> to supercritical pressure using existing MEA technology would be in the order of \$40, and the power output would be significantly reduced by the energy consumption in capturing and compressing CO<sub>2</sub>. The high capture cost and energy consumption would be a major barrier for implementing CO<sub>2</sub> mitigation methods. Alternative technologies may offer improvement. This paper reviews several separation technologies applicable to capture CO<sub>2</sub> from flue gas, and discusses improvement opportunities and research needs.

## INTRODUCTION

Concern over the increased concentration of CO<sub>2</sub> in the atmosphere and its effect on global climate change has increased the awareness and investigation for reducing CO<sub>2</sub> emissions. Most of the methods for mitigation require CO<sub>2</sub> in a concentrated form, while the CO<sub>2</sub> from fossil fueled power plants is mixed with nitrogen, water vapor, oxygen, and other impurities and has low concentrations (15 % for coal fired power plants, and less than 10 % for natural gas fired plants). Therefore, capturing CO<sub>2</sub> from flue gas is an important common link.

The current commercial operations for capturing CO<sub>2</sub> from flue gas use a chemical absorption method with Monoethanol Amine (MEA) as the sorbent. The method is expensive and energy intensive. An estimate by Pergman *et al* [1] using data from an ABB/Lummus Crest brochure [2] indicated the cost of capturing a ton of CO<sub>2</sub> including removing impurities and compressing CO<sub>2</sub> to a supercritical pressure would be in the order of \$40. While compression is an energy intensive and expensive component, the capture part of MEA method actually uses more energy and costs more than compression. The high capture cost is a major barrier for implementing near term carbon sequestration methods such as injecting CO<sub>2</sub> for enhanced oil recovery [1].

The other major shortcoming of the current technology is its high-energy consumption. The amine based method uses a large amount of low-pressure steam for sorbent regeneration, and the total power output is significantly reduced. It could lead to 20% reduction in electricity production for a PC plant (107MW/554MW) as a study by Booras and Smelser indicated [3].

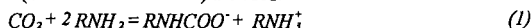
Following is a preliminary analysis of several separation technologies applicable to CO<sub>2</sub> capture, new power generation configurations that may simplify CO<sub>2</sub> capture, as well as a discussion of some improvement opportunities

## GAS SEPARATION METHODS APPLICABLE FOR CO<sub>2</sub> CAPTURE

Capturing CO<sub>2</sub> from the flue gas is essentially a gas separation process. Several separation methods, including Chemical Absorption, Physical Absorption, Physical Adsorption, Membrane Technologies, and Cryogenic Separation, can achieve such a goal. The judging criteria are capture effectiveness, process economy, energy consumption, and other technical and operational issues. Other measures such as modifying of power generation configurations by using O<sub>2</sub>/CO<sub>2</sub> Combustion mode and oxygen blown Gasification Combined Cycle, could alter the flue gas composition and pressure that could help the CO<sub>2</sub> capture. Such strategy has some benefit but also raises new technical challenges.

### Chemical Absorption

Chemical Absorption with MEA as the sorbent is currently used for separating CO<sub>2</sub> from flue gas [Eq.1]. This method was originally used for removing CO<sub>2</sub> from other gases such as methane, hydrogen, etc. Chemical absorption uses the different reactivities of various gases with sorbents to separate them. The reactions need be reversible so that the spent sorbent can be regenerated. For separating CO<sub>2</sub> from flue gas, chemical absorption appears appropriate because CO<sub>2</sub> is acidic and the majority of the rest of flue gas, nitrogen, is not. CO<sub>2</sub> can be absorbed by many basic sorbents including alkali carbonate, aqueous ammonia, and alkanolamines. The attention needs to be paid is how the sorbents can be regenerated. The binding between sorbent molecules and CO<sub>2</sub> generally is strong and this offers a fast and effective removal of most of CO<sub>2</sub> in one stage of absorption. However, the strong binding between CO<sub>2</sub> and the sorbent molecules is also one of the causes for high regeneration energy requirement. Second concern is the control of impurities and miner components in the flue gas including SO<sub>2</sub>, oxygen, etc. that may degrade the sorbents. These components have to be removed before the gas enters the absorber, or treated with appropriate measures. Lastly, because many sorbents are corrosive, only diluted solutions (around 18% for MEA) are used.



where R is the Monoethanol group. A schematic flow diagram is given at Figure 1.

In addition to the regenerator, a reclaiming operation is conducted periodically to recover amine by decomposing heat stable salts and to dispose of degradation products.

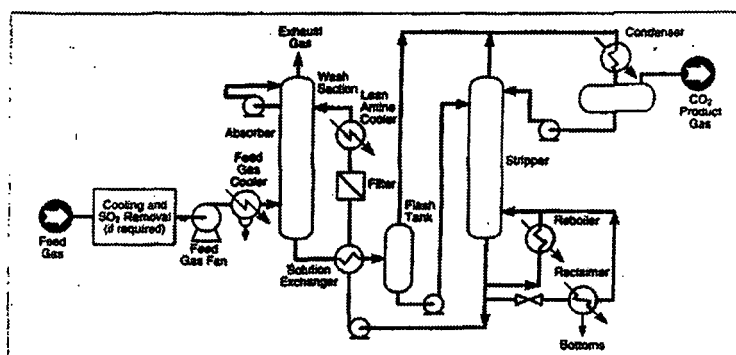


Figure 1. CO<sub>2</sub> Recovery Process Schematic Diagram [Ref. 2]

### Physical Absorption

In physical absorption, the gas  $\text{CO}_2$  molecules are dissolved in a liquid solvent, and no chemical reaction takes place. The binding between the  $\text{CO}_2$  molecules and solvent molecules, being either Van der Waals type or electrostatic, is weaker than that of chemical bonds in chemisorption. The amount of gas absorbed is linearly proportional to its partial pressure (Henry's law). Figure 2 gives the  $\text{CO}_2$  gas loading in several sorbents vs.  $\text{CO}_2$  partial pressure. The curves show linear relations between the partial pressure and  $\text{CO}_2$  loading for physical sorbents, and nonlinear relations for chemical sorbents. Thus the physical absorption is more effective when the partial pressure of the gas to be absorbed is high. The amount of gas absorbed also depends on the temperature. The lower the temperature, and more gas is absorbed (see methanol curves at different temperatures in Figure 2). Typical sorbents for  $\text{CO}_2$  are methanol, N-methyl-2-pyrrolidone, polyethylene, glycol dimethyl ether, propylene carbonate and sulfolane [6].

The desorption can be achieved either by lowering pressure as in the pressure swing absorption (PSA), or raising the temperature as in the temperature swing absorption (TSA). Physical absorption has been used in gas production processes [5] to separate CO<sub>2</sub> from hydrogen and CO. These processes include: Rectisol that uses methanol as solvent, Selexol that uses dimethyl ether of polyethylene glycol (DMPEG), Sepsolv that uses n-oligoethylene glycol methyl isopropyl ethers (MPE), Purisol that uses N-methyl-2-pyrrolidone (NMP), and Gasolan that uses N-methylcaprolactam (NMC).

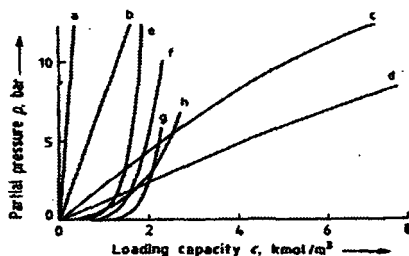


Figure 2. Equilibrium Curves of CO<sub>2</sub> in Various Solvents [Ref. 5]

Physical Absorption: a) H<sub>2</sub>O (30 °C); b) N-methyl-2-pyrrolidone (110 °C); c) Methanol (-15 °C); d) Methanol (-30 °C); Chemical Absorption: e) Hot potassium carbonate solution (110 °C); f) Sulfinol solution (50 °C); g) 2.5 molar diethanolamine solution (50 °C); h) 3 molar Amisol DETA solution.

### Physical Adsorption

In physical adsorption, gas is adsorbed on the solid surface by a Van der Waals force. Most important adsorbents are activated carbon, zeolite, silica gel, and aluminum oxide [4]. The separation is based on the difference in gas molecule sizes (Steric Effect), or different binding forces between gas species and the adsorbent (Equilibrium Effect or Kinetic Effect)[4]. Like physical absorption, two types of processes: Pressure Swing Adsorption and Temperature Swing Adsorption are used. Because the gas molecules are attached on the solid surface and form mono or multi-layers in *physical adsorption*, the gas loading capacity could be lower than in *physical absorption*, even though many adsorbents have large surface area per unit volume. Because of the large volume of CO<sub>2</sub> in the flue gas, it appears physical adsorption might not be an effective and economical solution for separating CO<sub>2</sub> from flue gas. The other limit in using physical adsorption for this purpose is the low gas selectivity of available sorbents [6]. However in combining with other capture methods, physical adsorption may become attractive. Such applications include membrane technologies.

### Membrane Technologies

Many membranes are made with similar materials used for physical adsorbents, because the physical quality, such as porous structure and selective gas affinity, are also useful for making membranes. Membranes are microscopic sieves. Under an applied pressure some molecules will pass through the micropores in membranes, and some molecules will be stopped.

The driving forces for gas separation using membranes are generally hydrostatic pressure and concentration gradient. There has been some work done in electrically driven separation of gases via ion conduction. Two types of membrane technologies can be used for separating CO<sub>2</sub> from other gases: *gas separation membranes* and *gas absorption membranes*. In using gas separation membranes a hydrostatic pressure is applied and the difference in permeability of gas species leads to separation of these gases. Although using separation membranes to separate CO<sub>2</sub> from light hydrocarbons has met with considerable success in the petroleum, natural gas and chemical industries, this technology may not be preferable to separate CO<sub>2</sub> from flue gas because of the large volume of the flue gas and the compression energy requirement. A study shows that a good separation using a two-stage system would cost twice much of the conventional amine separation processes [6].

In using gas absorption membranes, a liquid sorbent is used to carry away CO<sub>2</sub> molecules that diffuse through the membranes, and no high hydrostatic pressure is required. In this technology, the membranes serve as an interface between the feed gas and liquid sorbent. The membranes can be made in the forms of parallel hollow fibers, and feed gas and sorbent are moving on the opposite sides of the fibers. This configuration provides significantly greater liquid-gas contact area than packed absorbers, and can reduce the size, and possibly the cost of the absorber. Additional benefits include the independent control of gas and liquid flows, and minimization of flooding, channeling, or foaming of liquid sorbent in the absorber [6]. This configuration was under investigation by Norwegian researchers as a choice for offshore operation where the space and weight of the absorber are important factors. Considerable research is still required to

address issues such as how to deal with possible clogging of hollow fibers by fine particles in the flue gas.

### Cryogenic Separation

Cryogenic separation of gas mixtures uses the difference in boiling points of various gas species to separate them. Because all gas species have a distinctive boiling temperature, the cryogenic method can provide effective gas separation. The critical temperature and triple point of CO<sub>2</sub> are 31.6°C and -56.8°C respectively. Between these temperatures, CO<sub>2</sub> can be liquefied by compression and cooling. The major disadvantage of cryogenic method is the high-energy consumption and costs associated with gas compression and cooling. For CO<sub>2</sub> sequestration, liquid CO<sub>2</sub> is required in many cases, and the work spent on liquefying CO<sub>2</sub> is not wasted. However, since the concentration of CO<sub>2</sub> in flue gas is about 15% or less, the energy used to compress the rest 85% of flue gas is substantial. A simple calculation for the energy requirement for liquefying CO<sub>2</sub> by isothermally compressing the flue gas near the critical temperature to 74 bar would spend about 30% total power output in compressing 85% of the remaining gases, and this is about 50% more than MEA process. Methods to recover that amount of compression energy spent on 85% gas components could lower total energy consumption. Generally speaking, unless novel process schemes can be developed, cryogenic separation is an energy intensive operation.

### New Configurations

Reduction of capture cost may be achieved in new power plants by designs that integrate CO<sub>2</sub> capture with power generation. In oxygen/CO<sub>2</sub> combustion mode, the flue gas would consist of mostly CO<sub>2</sub>, and its capture is simplified. The oxygen production is also expensive and energy intensive, but the benefits from oxygen combustion including better thermal efficiency, reduction in the volume of flue gas and heat loss, and simplification or elimination of NO<sub>x</sub> control [6] can partially offset the costs. A more advanced configuration can be an oxygen-blown coal gasification combined cycle plant. In order to achieve more than 90% removal of CO<sub>2</sub> that would be emitted from the gas turbine by combusting the syngas, shift reactors are included to turn CO and water vapor to CO<sub>2</sub> and H<sub>2</sub>. In this configuration, CO<sub>2</sub> needs to be separated from H<sub>2</sub>. Because the gasifier operates at an elevated pressure, a physical separation, such as Selexol can be used. As no steam will be required to regenerate the sorbent, and no additional compression is required for the absorption process, the energy consumption for CO<sub>2</sub> capture is small. Booras and Smelser [3] indicated the energy consumption for 90% CO<sub>2</sub> removal together with compressing the captured CO<sub>2</sub> to a supercritical pressure would reduce power production by about 12%, and the majority of it is spent on compressing captured CO<sub>2</sub> to the supercritical pressure.

Because the existing oxygen production is energy intensive and will also generate a large amount CO<sub>2</sub>, efforts should be dedicated to the reduction of energy consumption in oxygen production such as developing oxygen separating membranes.

*As the vast majority of fossil power plants will not retire for many years, developing effectively CO<sub>2</sub> capture technologies applicable for existing plants is an urgent task. For those plants, because of the large volume of flue gas and the low partial CO<sub>2</sub> pressure, chemical absorption appears to be a rational choice, as compared with other method. Productive approaches in the near term would be tapping the potentials for improving the chemical absorption, incorporating new membrane technologies, and encouraging innovative ideas.*

### **DISCUSSION - IMPROVEMENT OPPORTUNITIES IN CHEMICAL ABSORPTION**

A major limitation of using MEA as a sorbent is its high heat of absorption with CO<sub>2</sub> (72 KJ/mole [8], equivalent to 18% of the combustion heat of carbon (393.5 KJ/mole)). Second, the concentration of MEA is used at 15 - 20%; this means energy has to be applied to heat the solution in the stripper and to evaporate some water. The total regeneration energy required is about 900 kcal/kg CO<sub>2</sub> [9] or 165 KJ/mole CO<sub>2</sub>, equivalent to 42% heat from burning a mole of carbon, and 25% of the total combustion energy generated by burning coal. Although the stripper uses a low grade steam and some heat it contains was not used for generating power anyhow, it still causes 20% reduction of power generation for a PC power plant. Several aspects should be explored to improve this process.

### Search for new sorbents

New sorbents that have high CO<sub>2</sub> loading capacity and lower heat of absorption should be studied. Some amines are less corrosive and can be used at a higher concentration. For example

Diglycol amine (DGA) can be used at 40% concentration thus has twice as much CO<sub>2</sub> loading capacity as MEA (currently used at 18%). A search should be directed to amines that have a lower heat of regeneration. Several sterically hindered amines have been examined and it is found that some hindered amines can reduce the heat of regeneration by 20 % [9]. Sterically hindered amines use geometrical effect to weaken the binding between the CO<sub>2</sub> and amine molecules. An alternative approach is to search for amines that have weaker chemical bindings with CO<sub>2</sub> molecules. Other non-amine sorbents and mixture of sorbents should also be evaluated.

#### Increase loading of sorbent

Increasing the amine concentration could reduce the amount of sorbent solution and the requirement of regeneration heat. Ref [10] indicated that regeneration energy requirement of a 50% MEA solution will be 40% lower than a 30% MEA solution. Additional benefits of using higher sorbent loading include reduced sorbent circulation, the size of reactors, and associated costs. Using higher series amines together with increasing the sorbent concentration may offer even better benefits. Regeneration energy requirements for a 50% MDEA (Methyldiethanolamine) solution would be 50 % less than those of a 30% MEA solution [10]. Current commercial restrictions on using higher MEA concentrations are related to excessive corrosion and solvent chemistry [10]. Assessment of the material requirements, performance of concentrated solutions, overall improvement in energy consumption, and costs need to be conducted.

#### Improve gas-liquid contact

Better gas-liquid contact can reduce the size of absorber and costs, improve practical CO<sub>2</sub> loading, and reduce the sorbent circulation and regeneration energy requirement. This becomes more important for new sorbents that have lower reaction rate constants along with their lower regeneration energy requirements. A study indicated that structured packing in an absorber can provide a much higher overall mass transfer coefficient than the currently used random packing [11]. Using the membrane technology can reduce absorber size because membranes provide large contact surface between the gas and liquid. A study indicated that an absorber using membrane technology can reduce its size by 72% and its weight by 66% compared with a conventional absorption column [12].

#### **SOME CURRENT EFFORTS IN THE US AND OTHER COUNTRIES**

Because CO<sub>2</sub> capture is critical for CO<sub>2</sub> sequestration, many countries are actively engaged in research in this area. Japanese researchers are testing various sorbents and have reported sterically hindered amines that save 20% in regeneration energy. Japan is also studying membrane materials to separate CO<sub>2</sub> from N<sub>2</sub> [13]. It has also reported a Cardo polyamide that has a higher selective permeability for CO<sub>2</sub>/N<sub>2</sub>, and hollow fiber membranes utilizing the Cardo polyamide were tested. In addition, a pilot plant with capacity of 1000 m<sup>3</sup>N/h (~30 TPD) was set up [7]. Canadian scientists at the University of Regina in Saskatchewan built a 1.77m high absorption column, and tested new sorbents and absorber packings [11]. The Norwegian efforts include increasing amine loading, testing new chemical sorbents, using hollow fiber membranes to reduce the size of absorber, modifying reactor designs for reducing corrosion, and reducing sorbent degradation [12]. In the Netherlands, hollow fiber membrane absorber and new sorbents were studied for capturing CO<sub>2</sub> for feeding a greenhouse [14].

The United States built the first commercial plant capturing CO<sub>2</sub> from flue gas using MEA for industrial application in Trona, California. Another facility in Poteau, Oklahoma used the similar technology to produce chemical grade and food grade CO<sub>2</sub> from flue gas. The National Energy Technology Laboratory (NETL) has initiated a study to improve the MEA-based absorption method. Current efforts include testing hindered amines and improving gas-liquid contact in the absorber. NETL has also supported studies of innovative approaches for capturing CO<sub>2</sub> including "CO<sub>2</sub> Capture from Industrial Process Gases by High-Temperature Pressure Swing Adsorption" by Air Products, "A Novel CO<sub>2</sub> Separation Systems" by TDA Research Inc., "Oxygen Enriched Combustion" By CANMET, and "CO<sub>2</sub> Separation using Thermally Optimized Membranes" by a team led by Los Alamos National Laboratory.

#### **SUMMARY**

##### Recognizing improvement potential

Present operations for separating CO<sub>2</sub> from flue gas are used for commercial CO<sub>2</sub> production in which the CO<sub>2</sub> can be utilized for producing a revenue (carbonation of liquids, enhanced oil recovery, etc.). The new demand from climate change concerns would stimulate research efforts to examine new opportunities. Capturing CO<sub>2</sub> for climate change also offers more flexibility

than industrial separation because high CO<sub>2</sub> capture and purity may not be necessarily required. Technologies not suited for industrial applications can still serve as a candidate for climate change concerns if the costs and energy consumption are favorable.

#### Improved chemical absorptions

A high priority in the near term would be tapping improvement potentials in chemical absorption to reduce the energy requirement. Significant reduction in cost and energy consumption could be achieved by studying new sorbents, increasing loading, improve gas/liquid contact, etc.

#### Physical absorption can be incorporated in advanced IGCC plants

Physical absorption can be effective when the partial gas pressure is high and the temperature is low. In integrating CO<sub>2</sub> capture in the power or fuel generation cycles, physical absorption will be a good choice. Examples include the O<sub>2</sub>-blown pressurized gasifier and combined cycles.

#### Collaboration with Industry

Capturing CO<sub>2</sub> for climate change poses a new challenge for the gas separation industry, and provides new incentives and opportunities. The progress made in improving CO<sub>2</sub> capture in turn will benefit other gas separations. There could be many potential collaborations between DOE sponsored research and industrial interests that would speed up the progress in developing advanced CO<sub>2</sub> capture technologies.

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